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Dual fluorescence of indole-2-carboxylic acid and indole-5-carboxylic acid

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Abstract Steady state spectroscopic studies on indole-2-carboxylic acid (I2C) and indole-5-carboxylic acid (I5C) show hidden dual fluorescence in the case of former in polar and nonpolar solvents whereas I5C shows distinct dual fluorescence in nonpolar solvents and broad structureless fluorescence band in polar solvent which is composed of two fluorescence bands. For both the molecules, the higher energy band has been assigned to be arising out from neutral form *i.e.* Franck-Condon excited state and the lower energy band seems to be arising out from proton transferred excited state. Detail work is going on

Keywords Fluorescence, phosphorescence, proton transfer

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Except for the case of dual fluorescence of azulene [1-3] and some other examples the excited state deactivation is governed by Kasha's rule [4], which states that fluorescence should come from the lowest singlet state provided excited state is non-reacting. Due to change in excited state geometry or any excited state reaction the phenomenon of dual fluorescence is generally attributed to twisted intramolecular charge transfer (TICT) [5,6], excited state proton transfer [7, 8] and also other different excited complexes [9, 10]. TICT state is caused by transfer of electron from one end of the molecule to the acceptor side producing maximum dipole moment at some twisted position. Excited state intramolecular proton transfer (ESIPT) is of much importance in fundamental and applied photochemistry. The majority of reactions of this type involve the transfer of a proton from an oxygen donor to an oxygen or nitrogen acceptor. An intramolecular proton transfer is facilitated in excited state if there is an intramolecular hydrogen bond between two moieties in ground state. Now, this communication will report results of the absorption and fluorescent properties of indole-2-carboxylic acid and indole-5-carboxylic acid. A detailed investigation on different aspects of emission and their mechanism is going on and would be a subject of future communication.

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The compounds Indole-2-carboxylic acid (I2 C) and Indole-5-carboxylic acid (I5C) were purchased from Aldrich Chemical, USA and were purified by vacuum sublimation. All spectral grade solvents Methylcyclohexane (MCH), Acetonitrile (ACN), Tetrahydrofuran (THF), Ethanol (EtOH) were used after vacuum distillation. The water used in this study is the milli pore water. All solvents were checked for absence of any fluorescence emission in the wavelength region of interest prior to preparing the solution. The absorption spectra at 300K were recorded with a Shimadzu absorption Spectrophotometer model UV-2101PC, and the fluorescence spectra were obtained with a Hitachi F-4500 Spectrofluorometer.

The absorption spectra of indole-2-carboxylic acid (I2C) and indole-5-carboxylic acid (I5C) shows broad structureless band in different organic polar and nonpolar solutions. The absorption spectra of I2C having peak in the region of (288-290) nm show solvent dependence, whereas the absorption spectra of I5C shows flat and broad absorption band having no trace of distinct peak (Figure 1). It is also important to note that in hydrocarbon solvent, I2C shows two shoulders in absorption band at 310 nm and 320 nm (Figure 1). In polar or hydroxylic solvent this shoulder vanishes producing more structureless broad band. If we compare this absorption spectra of I2C with the parent compound indole, we find a weak similarity between these two (Figure 1). This spectral change and appearance of lower energy shoulder in absorption spectra of I2C in hydrocarbon solvent results from 2-carboxylic acid substitution as well as from intramolecular hydrogen bonding between acid and basic group of the molecule. Also it is important to note here that this red shifted shoulder band in hydrocarbon solvent and structureless tail is accounted for the ground state close tautomeric form.

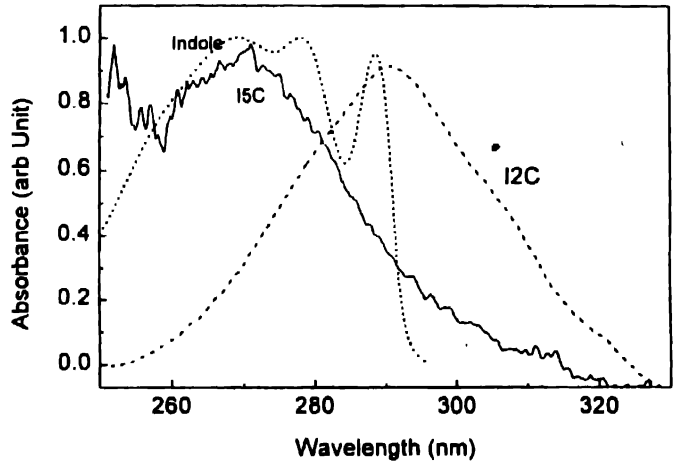


Figure 1. Absorption spectra of indole, indole-2-carboxylic acid and indole-5-carboxylic acid in methylcyclohexane (MCH) solvent respectively

We find a vast change in spectral distribution in absorption spectrum of I5C with respect to the absorption spectra of Indole. Irrespective of solvents properties, I5C shows flat bands (from 250-300 nm) with lower absorbance producing no sharp peaks (Figure 1). This change of absorption spectra is associated only with the redistribution of charge in excited state. So we can infer that the introduction of carboxylic group in 5 position of the parent molecule is responsible for this redistribution of charge through the intramolecular hydrogen bond formation between carboxylic group and basic group of the molecule in ground state.

Now, the difference in spectral behaviour of I2C and I5C is encountered by the distance of two intramolecular acid base moieties. Due to the increment of this moieties distance, ground state tautomeric form may be forbidden in I5C. This tautomeric form of I2C makes the difference between absorption spectra of two molecules.

Indole is highly fluorescing agent [11]. Indole 2-carboxylic acid (12C) shows moderately high fluorescence in room temperature on different solvents. In nonpolar hydrocarbon solvent the fluorescence spectra of I2C shows two distinct bands at 330nm and 350nm. But in polar solvent like ACN one could observe a strong band peaking at 365nm. In hydroxylic medium (ethanol) or in aqueous solution I2C shows the same stucturless broad fluorescence spectra like in ACN solution, Figure 2. In polar protic and aprotic solution, the higher energy band reduces and a broad band appears in 355–370 nm region. In comparison to the fluorescence

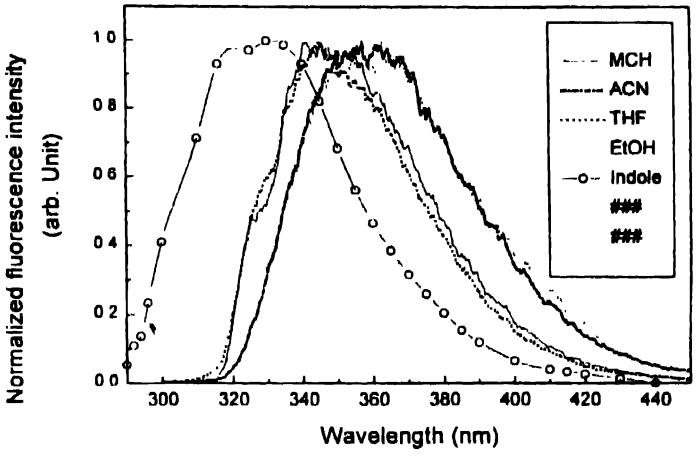
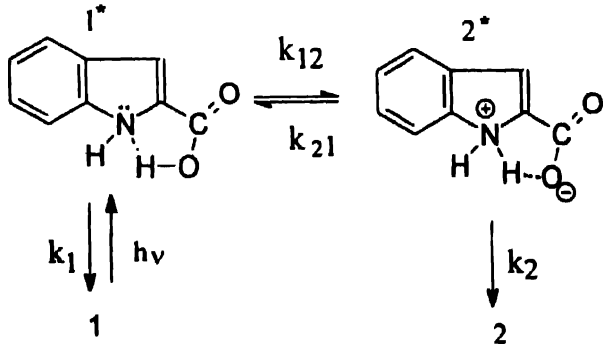


Figure 2. Fluorescence spectra of indole in ethanol solvent and fluorescence spectra of indole-2-carboxylic acid in different solvents

spectra of indole, the appearance of two bands in fluorescence spectrum of I2C in MCH solution points to a possible excited state proton transfer in hydrocarbon solution. The first higher energy band (330nm) is the normal fluorescence of indole, and second lower energy band is proton transfer band. Going to more polar solvent (ACN, DMF), the higher energy



Scheme 1.

band intensity reduces and lower energy band intensity increases, resulting a red shifted broad structureless emission spectra (Figure 2). The half width of the fluorescence spectra in all solvents is higher than that of the indole fluorescence spectra. Band shape analysis confirmed that the existence of two bands under the flat structureless fluorescence spectra of I2C. Comparing fluorescence spectra of I2C with the fluorescence spectra of indole we assign the two bands arising out of 1*(neutral form) and 2* [Scheme 1]. The red shift of envelope of band system on going from MCH to ACN may be thought as a consequence of larger stabilization of the zwitterionic form in excited state compared to the vertical ground state.

The organic hydroxylic solvent (ethanol) and water have large tendency to form intermolecular hydrogen bonding with each other and solute present within it [11]. But in this case no trace in fluorescence spectra of I2C have been found to detect the hydrogen bond formation with solvent molecules. So we can conclude that in hydroxylic medium, excited state intramolecular proton transfer occurs like other polar solvents supporting the Scheme 1.

In hydrocarbon medium, I5C exhibits distinct dual fluorescence on excitation by wide range of absorption band (Figure 3). The excitation spectra corresponding to the two peaks are

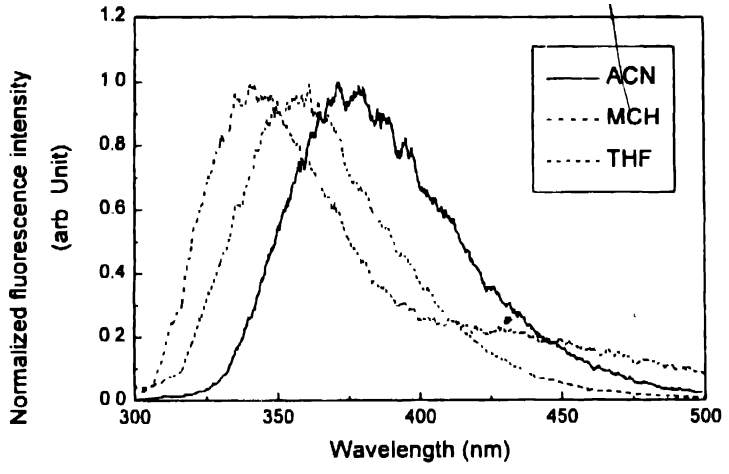


Figure 3. Fluorescence spectra of indole-5-carboxylic acid in different solvents

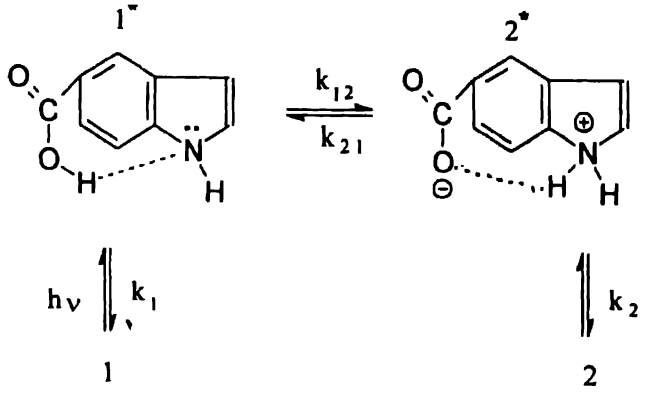
identical to each other and closely resemble the absorption spectra. This points that the origin of the two bands from the same excited state. In comparison to indole fluorescence spectra (Figure 2), the higher energy fluorescence band of I5C is assigned to the neutral fluorescence of indole group and lower energy band is due to excited state proton transfer. On placing the I5C in polar aprotic solvent, the lower energy emission increases and higher energy emission decreases producing a large envelope of total fluorescence. From band shape analysis, we see two distinct peaks, under the envelop of broad structureless emission spectrum which arise from neutral and proton transfer conformer (Scheme 2). The fluorescence emission spectra of I5C in different hydroxylic solvents, including water show the same large Stokes shifted bands which is composed of two hidden bands at 340 nm and 400nm region, with comparatively lower quantum yield, than other nonhydroxylic solvents. The addition of small amount of amine like triethyl amine (TEA) reduces the fluorescence intensity as well as quantum yield, keeping the band shape unaltered.

Now, considering excited state equilibrium between the neutral and double ionized form (zwitterionic form) according to Schemes 1 and 2 (for both the molecules), the excited state equilibrium constant k' can be defined by the ratio of concentration of 1* and 2* excited states :

$$k' = [2^*]/[1^*].$$

For steady state $k' = k_{12}/(k_2 + k_{21})$,

where k_1 and k_2 are decay rate of 1* and 2* whereas k_{12} and k_{21} are the proton transfer 1* → 2* and interconvertion rate constant 2* → 1*, respectively. If the back reaction is considerably faster than the decay of 2* ($k_{21} >> k_2$) k' becomes equal to the ratio of the interconvertion rate.



Scheme 2.

In I2C, the acid base groups are very close to each other than I5C. Hence we expect a faster back reaction (2* → 1*) in I2C resulting the lowering of second fluorescence band intensity. From our experiment we observed the same, *i.e.*, the second band intensity is higher in I5C than that of I2C. So in I2C, k' becomes equal to the interconvertion rates k' (k_{12}/k_{21}).

In nonpolar hydroxylic glass matrix at 77K, both the molecules are nonfluorescing. But in presence of triethyl amine (TEA), both the molecules behave as fluorescing species. The appearance of fluorescence and phosphorescence in presence of amine indicates that fluorescing species is mainly anionic in nature. But at 77k, both the molecule in ethanol glass shows fluorescence and phosphorescence. This observation indicates that in ethanol glass matrix the strength of intermolecular hydrogen bonding increases in I5C and intermolecular hydrogen bonding occurred in I2C which was hardly possible in room temperature. The intermolecular hydrogen bonding increases the anionic properties of the solute resulting the fluorescence and phosphorescence matrix. Judging the lifetime of the phosphorescence spectra in both matrices, we come to conclusion that the emitting triplet state of anionic form of both the molecules is (π, π^*) in nature.

References

[1] M H Hui, P De Mayo, R Suau and W R Ware *Chem. Phys Lett* **31** 257 (1975)

[2] Hans J Griesser and Urs P Wild *Chem Phys.* **52** 371 (1980)

[3] Urs P Wild, Hans J Griesser and V O Dinh Tuan J. F. M. Oth *Chem. Phys. Lett* **41** 450 (1976), J Den Blanken, G P Van Der Zwet and A J Hoff *Chem. Phys Lett.* **85** 233 (1982)

[4] M Kasha *Disc. Faraday. Soc.* **9** 14 (1950)

[5] P R Bangal, S Chakravorti and G Mostafa *J. Photochem. Photobiol. A Chem.* **133** 35 (1998)

[6] W Rettig *Angew Chem. Int. Ed. Engl.*, **25** 971 (1986)

[7] S J Formosinho and L G Arnaut *J. Photochem Photobiol. A Chem.* **75** 21 (1993)

[8] A Weller *Naturwis* **42** 175 (1995)

[9] H Leonhardt, A Weller and Ber Bunsen-Ges *Phys. Chem.* **67** 791 (1963)

[10] G J Kavarnos and N J Turro *J. Chem. Rev* **86** 401 (1986), A J Q Hoff *Rev Biophys.* **17** 153 (1984)

[11] L E Cramer and K G Spears *J. Am. Chem Soc.* **100** 21 (1978)